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Total and inorganic As in seafood products caught in an environment facing a mining and industrial area in Sardinia (Italy)

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INTRODUCTION

The Boi Cerbus lagoon, facing a mining and industrial site in Sardinia (Italy), is an important fishing area for the local population (Fig. 1). Previous studies showed high concentrations of total arsenic (As_{tot}) in fish, molluscs and crustaceans sampled in the lagoon, and a possible exceeding of the JEFCA PTWI value (*Provisional Tolerable Weekly Intake)* by some local consumer groups (teens and children) (1). However, the concentration of inorganic As (As_{inorg}) in the samples should be known for a correct assessment of potential risk, as its toxicity is much higher than that of the organic forms of arsenic.


Fig. 1. Boi Cerbus lagoon - Sardinia - Italy

SAMPLES AND ANALYTICAL METHODS

Eighty samples of 14 different species of fish, molluscs and crustaceans, sampled in the Boi Cerbus lagoon on 3 different seasons (winter, spring and summer 2013), were analysed for As_{tot} by ICP-MS and As_{inorg} by HPLC-ICP-MS (2). The operating scheme is shown in Fig. 2. The HPLC parameters and analytical conditions for ICP-MS are shown in Table 1 and 2, respectively.

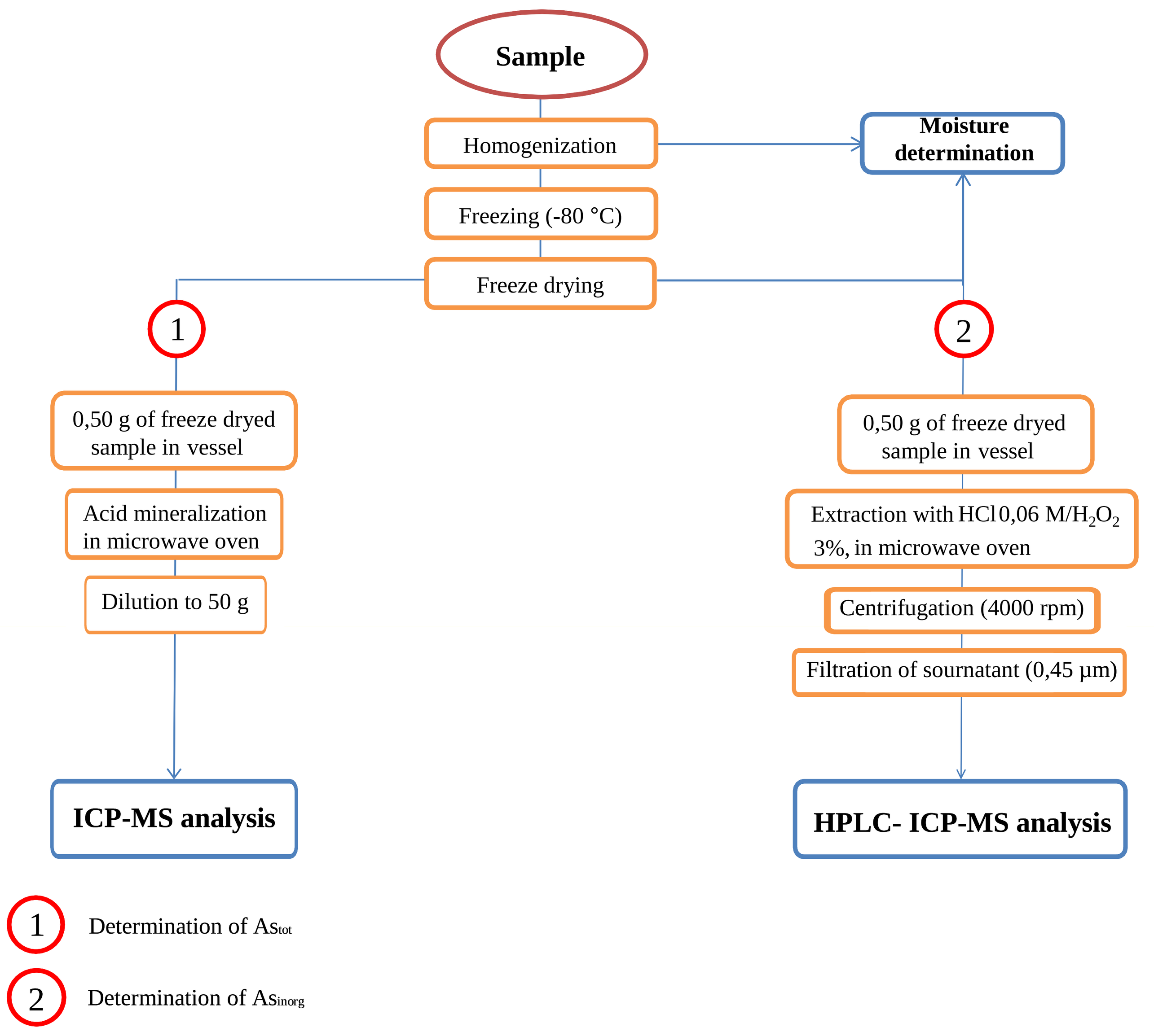

Fig. 2. Operating scheme for chemical analysis

Table 1. HPLC analytical conditions.

Instrument	*Perkin Elmer Flexar LC pumps*
Pump	Binary
Column	Anion exchange: Transgenomic ICSep ION 120, 120 x 4.6 mm
Column flow (ml/min)	1
Column oven temperature (°C)	30
Mobile phase	$(NH_4)_2CO_3$ 55 mM in 3% MeOH, pH ~ 10.3
Injection volume (µl)	25
Elution mode	Isocratic

Table 2. ICP-MS analytical conditions.

Instrument	*Perkin-Elmer SCIEX ELAN 6100DRC II*
Sample introduction system	
Nebulizer	Meinhard
Spray chamber	Quartz cyclonic
Plasma	
RF power (W)	1300
Carrier Ar flow (L/min)	0.9-1.1
Mass Spectrometry	
Dwell time (ms)	200
Sweeps/reading	20
Readings/replicate	1
Number of replicate	3
Scanning mode	Peak hopping
Monitoring mass	75
Internal standard	^{103}Rh (0.1 mg/L)

RESULTS AND DISCUSSION

Table 3 shows the mean values of As_{tot} and As_{inorg} for each species (+/- SD) and the percentage of As_{inorg}/As_{tot} in bivalves, gastropods, crustaceans and fish. Inorganic forms of As constitute in all cases only a small fraction of total As (max 1% in bivalves).

All the data were statistically processed to evaluate significant differences based on season, habitat and *taxon*, in preparation for a subsequent risk assessment. The Kruskal-Wallis test showed no statistically significant differences among the three seasons, nor for the concentrations of total arsenic (p = 0.2549), nor for the average percentage of the As_{inorg}/As_{tot} (p = 0.0817). The 14 species were divided into two clusters: benthic organisms (Olive green cockle, Banded murex, Mediter. shore crab, Gobies, Combtooth blenny and Common sole) and nektonic organisms (Big-scale sand smelt, Salema, Grey mullets, Gilthead sea bream and European seabass), to evaluate the possible influence of habitats. Using the non-parametric test of Mann-Whitney, the difference between the average levels of As_{tot} in benthic organisms (38.53 ± 5.21 mg/kg) and in nektonic ones (4.89 ± 0.80 mg/kg) was statistically significant (p <0.0001). With regard to average percentage of As_{inorg}/As_{tot}, a not statistically significant difference (p = 0.1038) was observed between benthic organisms (0.21% ± 0.04%) and nektonic ones (0.02% ± 0.01%), using the same nonparametric test. The same species were grouped according to the *taxon* into two new clusters: invertebrates (Olive green cockle, Banded murex, Mediter. shore crab) versus vertebrates (all the other species). According to the Mann-Whitney test, the difference between the average levels of As_{tot} in invertebrates (52.56 ± 7.46 mg/kg) and vertebrates (9.75 ± 1.33 mg/kg) was statistically significant (p <0.0001). Differences due to habitat and *taxon* variability are probably both significant, although currently we are not able to accurately assess the contribution of each one.

The difference in mean percentage of As_{inorg}/As_{tot} between invertebrates (0.31% ± 0.06%) and vertebrates (0.03% ± 0.01%) was statistically significant (p = 0.0002).

Despite the very high concentrations of As_{tot} detected in some aquatic species, the values of As_{inorg} were in all cases low, even if with different concentrations, due to species-specific characteristics in the metabolism of the element. Therefore a risk assessment based only on the values of As_{tot} can lead to incorrect conclusions.

Table 3. Total and inorganic arsenic mean concentrations (mg/kg w.w. ± S.D.) and their ratio.

Scientific name	*FAO nomenclature*	*Sample type*	*N*	*As_{TOT}*	*As_{INORG}*	*As_{INORG}/As_{TOT} %*
Cerastoderma glaucum	Olive green cockle	Bivalve mollusc	11	15.5 ± 2.6	0.11 ± 0.03	0.74 ± 0.22 %
Phyllonotus trunculus	Banded murex	Gastropod mollusc	10	106 ± 24	0.011 ± 0.012	0.01 ± 0.01 %
Carcinus aestuarii	Mediter. shore crab	Crustacean	10	40.0 ± 12.6	0.054 ± 0.054	0.14 ± 0.14 %
Gobius niger jozo	Black goby	Fish	8	16.6 ± 4.9	0.001 ± 0.001	<0.01 %
Zosterisessor ophiocephalus	Grass goby	Fish	3	34.3 ± 5.7	0.004 ± 0.003	0.01 ± 0.01 %
Solea vulgaris	Common sole	Fish	6	15.4 ± 5.7	0.001	<0.01 %
Sparus aurata	Gilthead seabream	Fish	3	15.2 ± 1.9	0.001	0.00 %
Anguilla anguilla	European eel	Fish	3	6.6 ± 5.7	0.001	0.01 ± 0.01 %
Mugil cephalus	Flathead grey mullet	Fish	6	5.2 ± 1.2	0.002 ± 0.002	0.05 ± 0.04 %
Liza aurata	Golden grey mullet	Fish	6	3.7 ± 1.1	0.001 ± 0.001	0.02 ± 0.02 %
Atherina (Hapsetia) boyeri	Big-scale sand smelt	Fish	4	3.0 ± 0.7	0.001	0.04 ± 0.04 %
Salaria basiliscus	Combtooth blenny	Fish	3	2.6 ± 1.7	0.007 ± 0.002	0.33± 0.15 %
Dicentrarchus labrax	European seabass	Fish	5	2.0 ± 1.0	< LOD	<0.01%
Sarpa salpa	Salema	Fish	2	0.49 ± 0.07	< LOD	<0.01%

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